GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO. _____

Project No. E-19-656 DATE 6/14/82

Project Director: Dr. Pradeep K. Agrawal School/Lab ChE

Sponsor: Dow Chemical Co.; Midland, Michigan 48640

Type Agreement: Standard Industrial Agreement dated 6/1/82

Award Period: From 6/1/82 To ~~5/31/83~~ 9/3/83 (Performance) 6/10/83 (Reports)

Sponsor Amount: $20,902 Contracted through:

Cost Sharing: $6,975 (E-19-324) GTRI/~~GKK~~

Title: Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts During Reduction of Low Molecular Weight Nitriles

ADMINISTRATIVE DATA OCA Contact Linda H. Bowman x4820

1) Sponsor Technical Contact:

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Defense Priority Rating: none Security Classification: none

RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with none proposed

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 11/1/83

Project No. E-19-656 School/~~Lab~~ XXX Ch E

Includes Subproject No.(s) N/A

Project Director(s) Dr. Pradeep K. Agrawal GTRI/~~XXX~~ XXX

Sponsor Dow Chemical Company

Title Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts During Reduction of Low Molecular Weight Nitriles.

Effective Completion Date: 9/3/83 (Performance) 9/13/83 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [X] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [X] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

Continues Project No. N/A

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E-19-656

Georgia Institute of Technology

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ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING
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September 7, 1982

Dr. Ed Vrieland
Central Research, 1776 Building
Chemical Process Laboratory
The Dow Chemical Company
Midland, Michigan 48640

Dear Ed:

This is to bring you up to date on the progress made during the first quarter (June 1, 1982 - August 31, 1982) on the project entitled "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of Low Molecular Weight Nitriles." The results obtained during this period have been rather unexpected, but I hope you will agree that they are quite interesting. During the period of summer, 1982, Mr. Scott McMillan has been working full-time on this project, and he is preparing a major report on the findings of these experiments. I will send you a copy of this report by the end of September, 1982. The results presented here briefly describe the main thrust of our work.

Since submitting our last progress report in April 1982, we started experimenting with Pt-Au bimetallic catalysts. Initial runs were made using coimpregnation technique. However, the results of reaction studies indicated that the presence of Au on catalyst has no effect either on the activity or on the selectivity of Pt/Al_2O_3. This behavior was as expected since Pt-Au do not form alloy when prepared by coimpregnation procedure (de Jongste, H. C., Kuijers, F. J., and Ponec, V., in "Preparation of Catalysts", eds. B. Delmon, P. A. Jacobs, and G. Poncelet, pp. 209, Elsevier, 1976). As suggested in another study (O'Cinneide, A., and Gault, F. G., J. Catal. 37, 311 (1975)), repeated cycles of oxidation (at 77°C) and reduction (at 800°C) were attempted over coimpregnated catalysts to achieve alloying between Pt and Au but with no apparent success. The Pt-Au alloy catalysts were prepared by using coreduction method (Kulifay, S. M., J. American Chemical Society, 83, 4916 (1961); a copy of the paper is enclosed). The coreduction involves dissolving the two metals in aqua regia and adding this solution slowly to a suspension of silica in an aqueous solution of hydrazine hydrochloride and ammonia. The mixture is heated for one hour at 80°C, filtered and washed with water and methanol, and then dried at 100°C. The catalyst prepared by coreduction method was tested in the reactor, and severe activity reduction (by more than an order of magnitude) was observed depending upon the Au/Pt ratio; the amount of Au was varied to give up to 1:1 atomic ratio. However, in all cases the selectivity of alloy catalysts was worse than that of Pt catalysts alone: almost no traces of butyl amine were visible, the major reaction product was butane with small amounts of dibutyl amine and tributyl amine.

While these findings were contrary to our earlier expectations, they were nevertheless interesting. The fact that an activity drop by ten-fold or more was observed due to the presence of Au, indicated strong interaction (alloying) between Pt and Au. However, such a phenomena should also lead to reduced ensemble size which should enhance the formation of butyl amine if the observations made with C-C bonds are to hold true for the C-N bonds. These apparently contradictory results led us to rethink our approach. We realized that we had no information on how the activity and selectivity of Pt catalysts was influenced by the Pt crystallite size.

Subsequently, the work was focused towards the effects of Pt crystallite size. The catalysts studied previously in the reactor were characterized using X-ray line broadening technique. Although these experiments did not provide quantitative information on the crystallite size due to the small loadings (one wt. percent or below) of Pt, they indicated, however, Pt crystallites greater than $\sim$ 50 A^o because this is the limit of detection by x-ray diffraction procedures. Hence, an attempt was made to obtain metal particle size information using H_2 chemisorption measurements and transmission electron microscopy (TEM). The characterization using TEM was performed at the Engineering Experiment Station laboratory of the Georgia Institute of Technology. The preparation of samples for TEM study involved polymerization in polymethyl methacrylate and then cutting the specimens using ultra-tome with a diamond knife; the thickness of these specimens is about 800 - 1000 A^o. The detection limit for Pt particles is about 80 A^o; the particles below 80 A^o may not be observed. The results obtained using TEM are enclosed here, and two observations are in order: (i) the catalysts which were not calcined between impregnation and reduction step have generally smaller crystallites than those catalysts which were calcined, and (ii) similar catalyst preparation method leads to wide variations in crystallite size depending on the support. For example, for calcined catalysts, 1% Pt/MgO had metal crystallites in the range of 200 - 300 A^o; 1% Pt/SiO_2 had metal crystallites in the range of 100 A^o and below; and 1% Pt/Al_2O_3 had all Pt crystallites below 80 A^o. It is interesting to note that magnesia-supported Pt catalyst has the largest particle size, and it also has the highest selectivity for the formation of butyl amine.

The Table I below compares the activity and selectivity of uncalcined vs. calcined catalysts for all three supports. Two main observations can be made: (i) the activity of uncalcined samples is about an order of magnitude higher than that of calcined samples, and (ii) the selectivity for hydrogenation products is greater on uncalcined catalysts than on calcined catalysts. One point must be mentioned here: this increase in selectivity is not due to an increase in the formation of butyl amine but rather due to the formation of dibutyl amine and tributyl amine. Although it would be premature to make firm conclusions at this point while we are still in the middle of our study, we do wish to speculate as follows: (i) larger crystallites of Pt lead to the formation of the primary product - butyl amine, and smaller crystallites result in the formation of butane, and (ii) the changes observed in the selectivity behavior of calcined vs. uncalcined catalysts may not necessarily be related to the crystallite size but may be related to the total chlorine content. There may be less chlorine on uncalcined catalysts.

Our next few experiments will be conducted using Pt black to confirm these speculations and to see whether the role of support is only in changing the particle size. I will keep you posted with the results of our investigation.

With kind regards.

Yours sincerely,

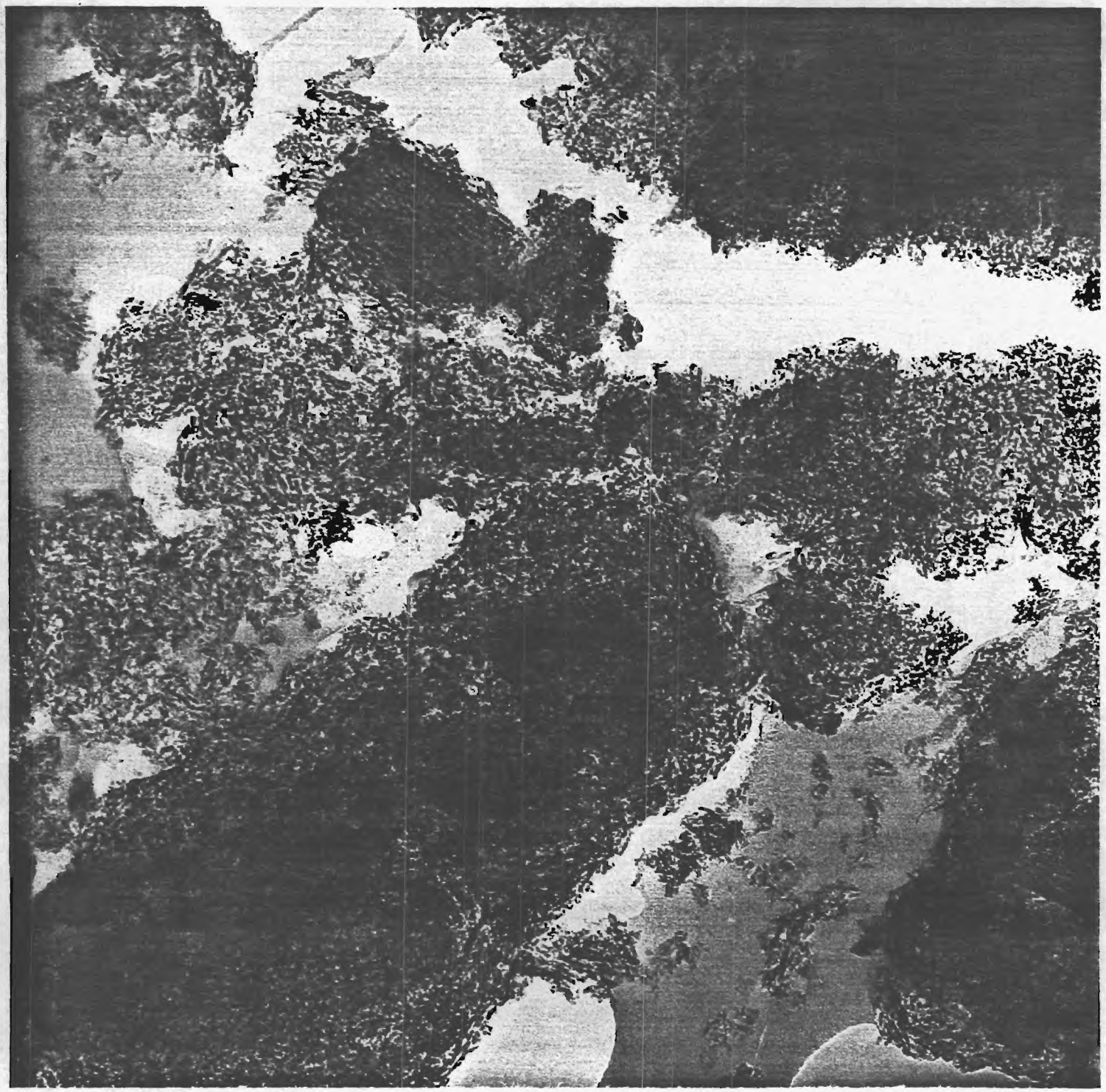
Pradeep K. Agrawal
Assistant Professor

PKA:law

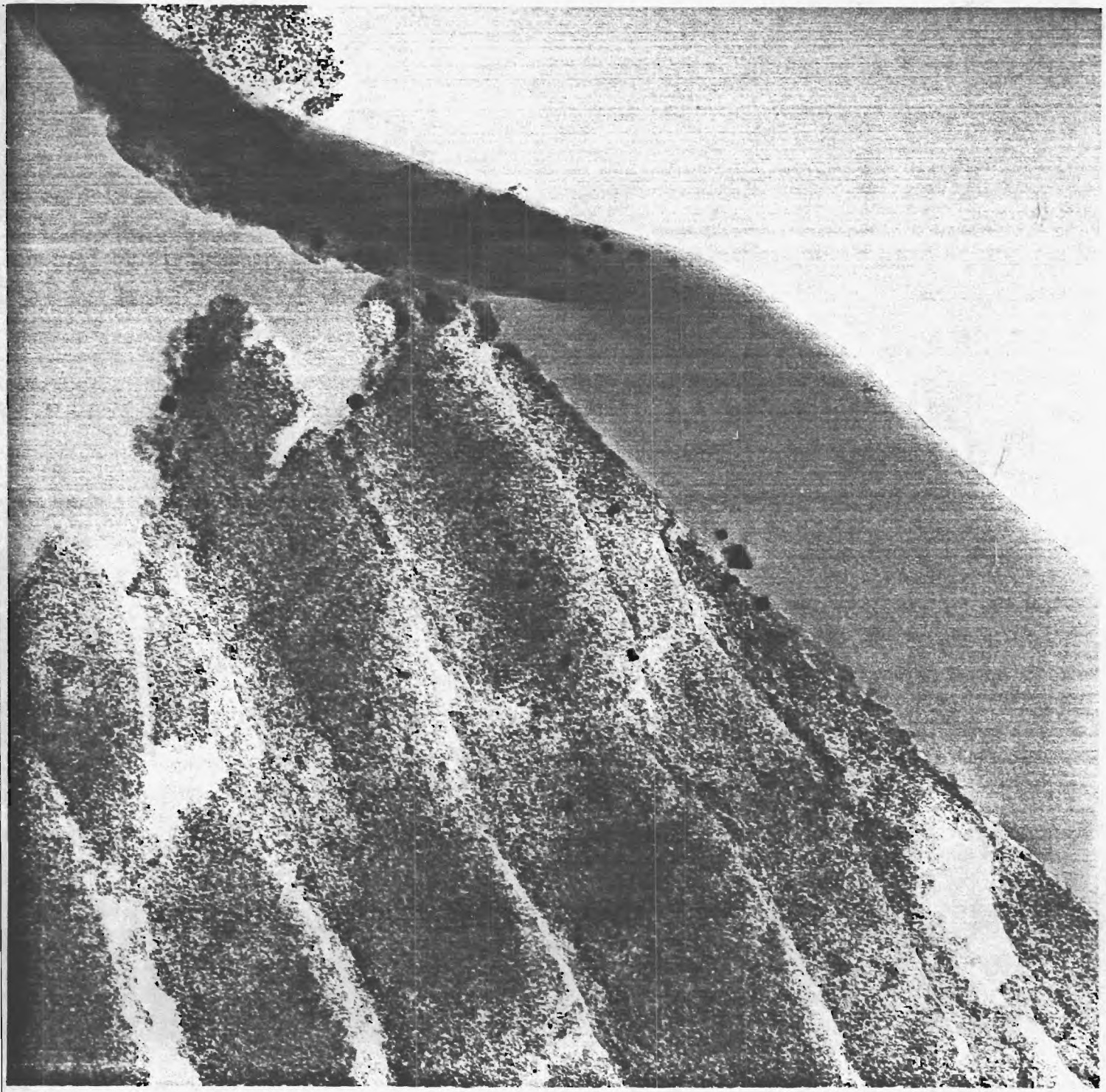
Table I

Catalyst	Catalyst Activity*, $\frac{\text{gmoles Butyronitrile}}{\text{g Cat - hr}}$		Selectivity, $\frac{r_{Hyd}}{r_{Hyd.}+r_{Cra}}$	
	Calcined	Uncalcined	Calcined	Uncalcined
1% Pt/SiO_2	0.0043	0.1273	41%	61%
1% Pt/Al_2O_3	0.0109	0.0964	61%	90%
1% Pt/MgO	0.0083	--	78%	--
0.5% Pt/MgO	--	0.0266	--	91%

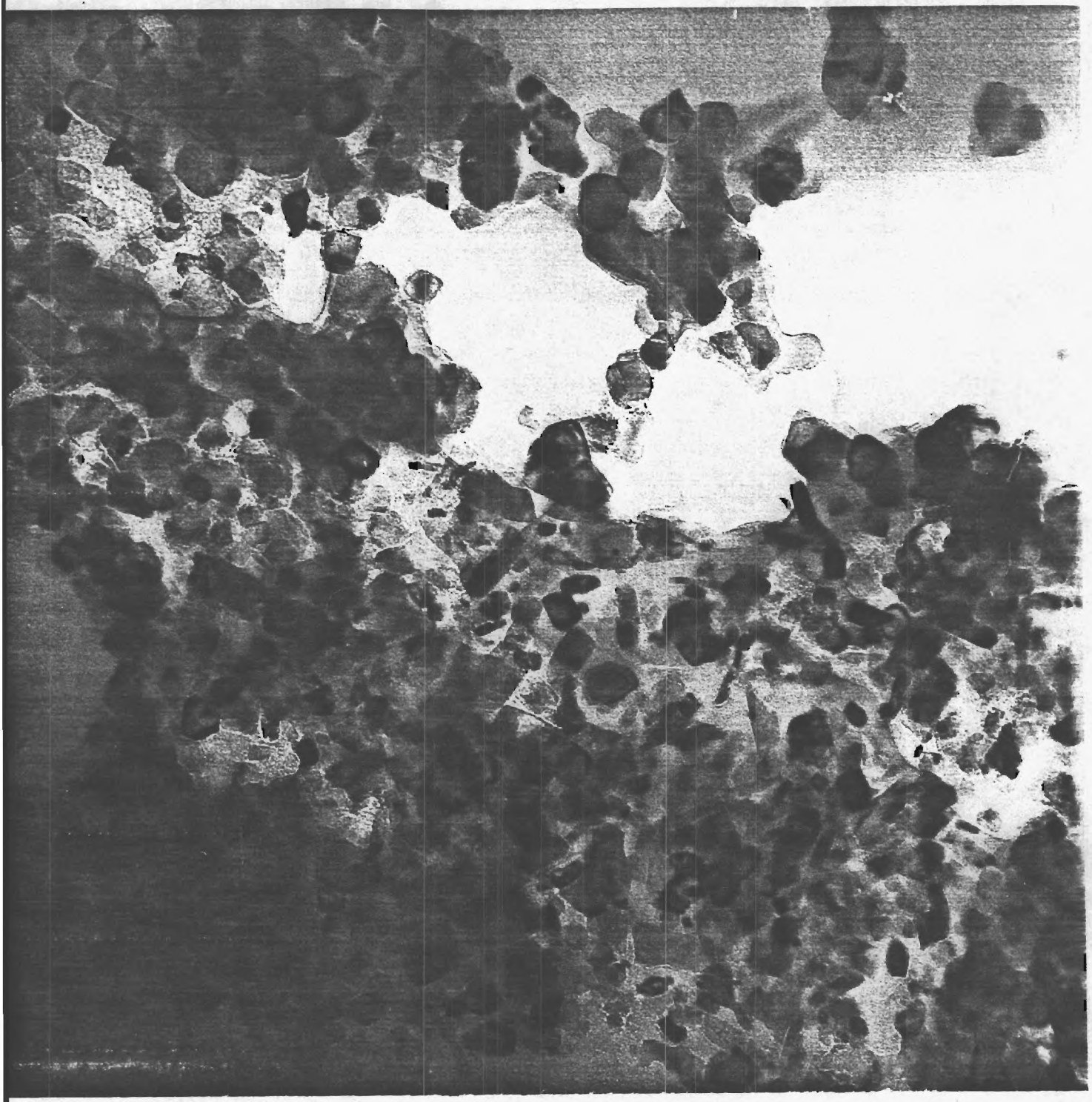
*at 200°C



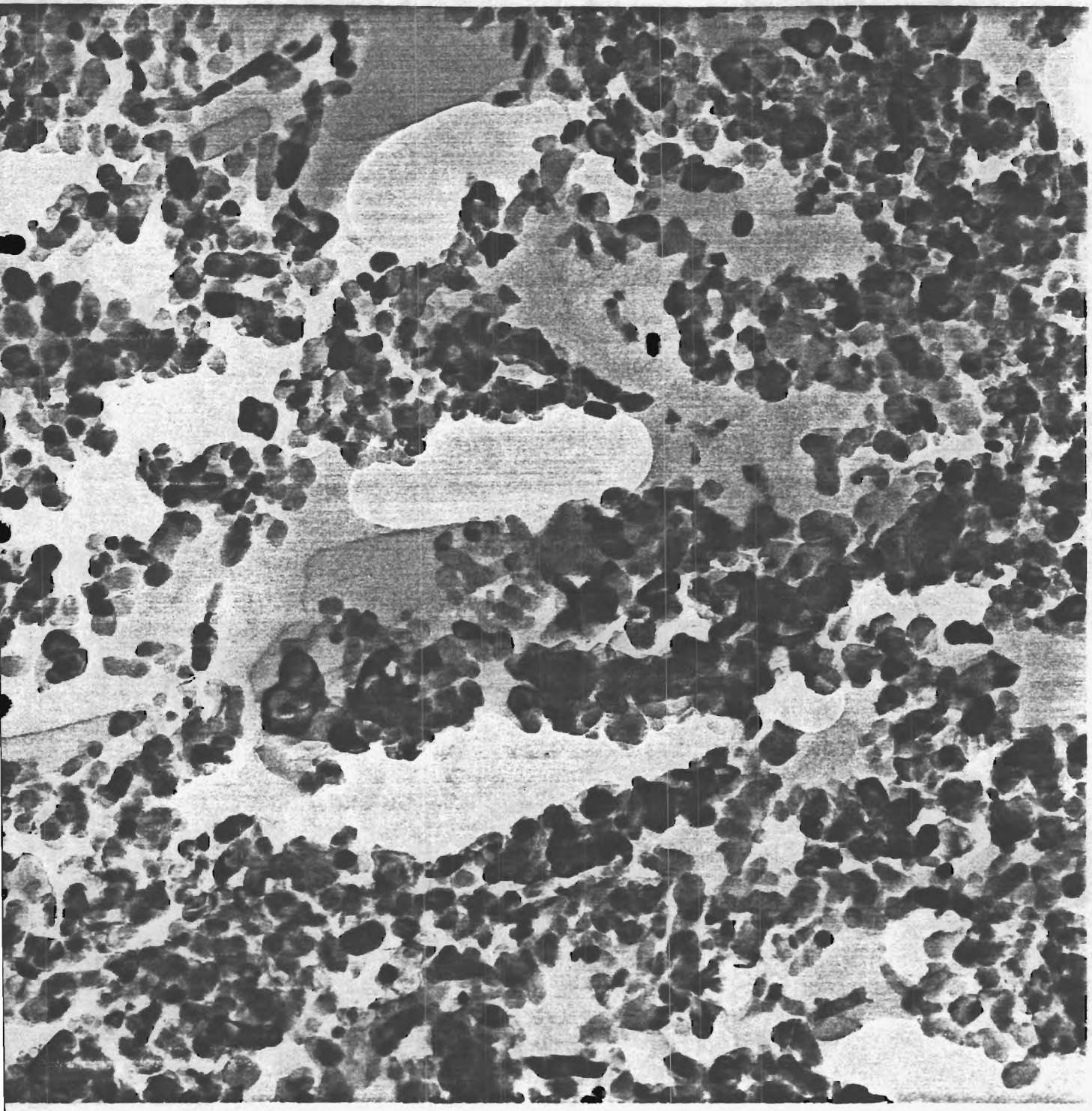
1% Pt/Al_2O_3, calcined in air at 550 °C after impregn. and prior to reduction



1% Pt/SiO_2, calcined in air at 350°c after impregnation & prior to reduction



1% Pt/MgO, calcined in air at 350°C after impregnation and prior to reduction



% Pt in MgO, not calcined after impregnation 154 KX

1% Pt/SiO_2 , uncalcined

E19-656

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SCHOOL OF
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December 6, 1982

Dr. Ed Vrieland
Central Research, 1776 Building
Chemical Process Laboratory
The Dow Chemical Company
Midland, MI 48640

Dear Ed:

This is the second quarterly progress report on the project entitled "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of low Molecular Weight Nitriles", covering the period 9/1/82 to 11/30/82. The work during these three months has been directed towards gaining a better understanding of the role of support in affecting catalyst activity and selectivity. Although we have faced several difficulties with the experimental apparatus (as mentioned below), but we have obtained very interesting results and some new insights into the catalytic system. The main among experimental difficulties has been the Gas Chromatograph Analytical System. It appears that the GC column (carbopak B/4% carbowax 20M/0.8% KOH) provides good separation and a stable baseline only for a period of 2-3 months (we have replaced four sets of GC columns during the last 12 month period). This problem is mainly because of the extreme temperature limit (220°C) that we have to go to in order to separate tributyl amine. The columns, which we replaced in the last week of October, are not separating higher amines at present and we are still working in this area. The other problem has been the breakdown of our H_2 chemisorption apparatus. We have ordered the components to build another apparatus and it should be operational before the end of January, 1983.

We have studied the nitrile hydrogenation reaction over (1) Pt black, (2) oxidized Pt powder, (3) 50-50 wt. percent mixture of Pt black and MgO, and (4) 50-50 wt. percent mixture of Pt black and SiO_2. The results for Pt black-SiO_2 mixture were not quantitative due to analytical problems, so I will describe them here only qualitatively. The results for the other three catalysts are compared in Table I with the other supported catalysts, which have been communicated to you earlier. Since, we haven't measured the surface area of Pt black due to the breakdown of Micromeritics apparatus, the rates are calculated on the basis of per unit gram of Pt; for both supported and unsupported catalysts. Hence, instead of absolute rates of reaction, it would be more appropriate to compare the data on product distribution and selectivity (Table I).

On Pt black (metal reduced at 350°C for 12 hr in UHP H_2), the observed selectivity is 99%, the highest we have seen in any run. Also, the major hydrogenation product is butyl amine (80% butyl amine. 20% dibutyl amine). The second row in Table I shows the data for Pt black powder which has been oxidized at 350°C for 12 hours in a 4% O_2 (balance He) stream; the observed selectivity for oxide catalyst is only 56%. Moreover, there is no formationof higher amines. The total activity has increased 2-fold, with most of this increase attributed to a 68-fold increase in the rate of cracking (butane formation). The third row (Table I) shows the behavior of a 50-50 weight percent mixture of Pt black and MgO which has been treated with H_2 at 350°C for 12 hours. The product distribution is similar to that observed in the absence of MgO; however, the nitrile conversion has increased about 3.5-fold. The results for mixture of SiO_2 and Pt black are not included in Table I, because there were analytical problems in separation. However, very poor selectivity (and significant butane formation) was observed, matching the performance with silica-supported Pt catalysts.

Based on the above results, the following observations are in order:

1. Significant amount of cracking (butane formation) takes place on PtO catalyst, and hence a poor selectivity can be expected on not-well-reduced catalysts.

2. Dibutyl formation appears to be formed on metallic Pt but not on PtO.

3. The carriers (SiO_2, Al_2O_3, MgO) appear to be involved in the hydrogenolysis of butyl amine to yield butane and ammonia. The results indicate the possibility of H_2-spillover effect.

The first and second observations are supported by the results shown in the first two rows of Table I. Another supporting evidence comes from the data for supported metal catalysts. The supported catalysts which were reduced (with no calcination) gave much larger amounts of dibutyl amine than the ones which were calcined and then reduced. It appears that the calcined catalysts were not reduced completely by 350°C H_2 treatment. Also, it should be noted (Annual report, March, 1982) that the catalysts reduced at 500°C gave higher selectivity than those reduced at 350°C, evidently due to increased formation of dibutyl amine. The H_2-spillover effect is indicated by a 4-fold increase in the activity of catalyst bed when MgO is added to the Pt black. A five-fold increase in the activity of Pt for benzene hydrogenation has been reported in the presence of ν-Al_2O_3 (Antonucci, et al., J. Catal. 75, 140 (1982)). Moreover, this effect is observed to be temperature-independent in the range of 60°C to 110°C (a copy of this paper is enclosed). In the absence of spillover effect, one can explain the strong adsorption of amines over carrier, but how can one explain the hydrogenation of amine to hydrocarbons is not clear. Nevertheless, this point needs to be investigated in more detail. For the near future, we plan to focus on the following points:

1. Characterize the rate and selectivity of Pt vs. PtO more carefully over a broad temperature range. Also, conduct temperature-programmed reduction studies of the Pt catalysts supported on different carriers to see if there is a significant effect of carrier on the reducibility of Pt.

2. Focus on one support only, i.e., MgO. Prepare Pt/MgO catalysts with varying degree of dispersion and study the reducibility of Pt as a function of crystallite size using TPR and correlate it with the rate selectivity behavior. We have got to understand the behavior of one catalyst (Pt/MgO) before moving on to other supports or bimetallics.

3. We also plan to conduct a more detailed study of the role of support in mechanical mixture forms. For example, a distinction can be made between the catalyst bed (well-mixed MgO and Pt black powder) and two beds (the first of Pt black and the second one of MgO, both separated to minimize the effect of spillover).

Please call me if you have any questions or comments.

With regards.

Yours sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA:law

cc: Mr. Scott McMillan

Table I

Rates of cracking and hydrogenation at 200°C, 1 atm; feed consists of 10% butyronitrile (balance H_2)

Catalyst	Pretreatment	Rate of butyronitrile conversion, gmoles Butyronitrile/gm Pt-hr					Selectivity
		Butane	Butyl Amine	Dibutyl amine	total hydrogenation	total cracking	
Pt black	H_2 at 350°C 12 hr	0.0022	0.1307	0.0732	0.2039	0.0022	0.99
Pt black	4% O_2/He at 350°C, 12 hr	0.1502	0.1902	--	0.1902	0.1502	0.56
Pt black/MgO 50/50	H_2 at 350°C 12 hr	0.0145	0.3036	0.3566	0.6602	0.0145	0.98
1% Pt/MgO	Calcined, H_2 at 350°C, 12 hr	0.23	0.83	--	0.83	0.23	0.78
1% Pt/MgO	H_2 at 350°C 12 hr	2.07	7.43	3.28	10.71	2.07	0.84
1% Pt/Al_2O_3	Calcined, reduced at 350°C	0.45	0.07	0.68	0.75	0.47	0.61
1% Pt/Al_2O_3	reduced at 350°C	0.90	0.25	6.7	9.65	1.15	0.89
1% Pt/SiO_2	Calcined, reduced at 350°C	0.61	0.43	--	0.43	0.61	0.41
1% Pt/SiO_2	reduced at 350°C	6.15	3.07	7.44	12.73	8.2	0.61

E-19-656

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

March 5, 1983

Dr. Ed Vrieland
Central Research; 1776 Building
Chemical Process Laboratory
The Dow Chemical Company
Midland, Michigan 48640

Dear Ed:

This is the third quarterly progress report on the project entitled "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of Low Molecular Weight Nitriles", covering the period 12/1/82 to 2/28/83. The main focus of our work during this period has been to eliminate the problems which were discussed in the second quarterly progress report. In the last two weeks we were able to conduct some reaction studies, the results from which are also presented below.

The first and most troublesome difficulty was in the GC analysis. We had been using (carbopak B/4% carbowax 20M/0.8% KOH) column packing for the separation of butane, butyronitrile, butyl amine, dibutyl amine, and tributyl amine. It was found that the columns lasted for only about two months before irreversible degradation in their performance; dibutyl amine and tributyl amine could not be separated. Since we were using glass columns which were purchased from Suppelco, it put severe constraints on the time and cost. Now, we have replaced the packing with a new one (10% Apiezon L/2% KOH on 80/100 Chromosorb® WAW) which separates the components on the basis of their boiling point. The column is packed in-house using a 6 ft x 1/8 inch ss column. The column is initially held at 50°C for 2 min., and then the temperature is increased to 170°C linearly at a rate of 8°C/min. The butyl amine and the butyronitrile are baseline separated; the total analysis time is ~ 19 min. (which is the elution time for tributyl amine). However, this column does not separate light gases (H_2, NH_3, and butane). Hence, a second column (4 ft x ¼ inch ss) packed with neutral alumina is used for butane analysis (elution time ~ 4 min). Both columns are arranged in such a way that the sample injection can be made to either column. Also, while one acts as a separation column, the other one acts as a reference column. The sensitivity of analysis is as good as it was with the older column.

The second difficulty appeared in our feed system. For feeding butyronitrile, we were using Sage® syringe pump. Over a period of almost 18 months, its performance deteriorated in that butyronitrile concentration in the feed oscillated by as much as a factor of two. We speculate the problem to be due to wear off in the gear box assembly. However, the performance characteristics of the pump were such that the concentration of butyronitrile could not be varied over a wide range. While the syringe pump worked satisfactorily for the exploratory work and preliminary screening of catalysts, we had realized that it will have to be replaced by another system for kinetic studies. The modified feed system is shown in Figure 1. Here, H_2 gas is dispersed into the liquid reactant via a fritted glass disc. As the gas bubbles rise through the liquid, the gas becomes saturated in nitrile and is then passed over the catalyst. The feed concentration can be maintained constant over a period of 12 hours (within 1% error). In addition, the concentration can be varied either by changing the H_2 flow rate or by changing the water bath temperature in which the saturator is immersed. Table 1 shows the effect of bath temperature; a temperature variation between 0 and 50°C can cause a ten-fold change in the concentration of butyronitrile without affecting the residence time in the reactor. A change in H_2 flow rate would bring even greater range of butyronitrile concentration. We are quite pleased with this modification as it will greatly aid us in obtaining more quantitative data and in performing careful kinetic studies.

To test this feed system, we have carried out reaction measurements at several concentrations of butyronitrile using uncalcined 1% Pt/MgO catalyst. The steady-state activity and selectivity results are shown in Figure 2. A positive order dependence of rate on the butyronitrile concentration is seen, whereas no definite pattern exists for cracking reaction. These experiments were performed simply to test the feed system and we do not wish to place excessive confidence in the quantitative nature of these results. We will be conducting more studies in the future.

We have also conducted reactor studies in which a mixture of butyronitrile and He was passed over the MgO bed; no change in feed was observed. In another study, a mixture of butyronitrile and H_2 was passed over the MgO bed, and, again, no activity was observed. Similar observations were made when feed consisted of butyronitrile, butyl amine, and H_2. We believe that MgO as a support is inert in the reaction, at least in the absence of platinum. Finally, we tested a mixture of butyronitrile and butyl amine (0.24% butyronitrile, 7.55% butyl amine) in He over 1% Pt/MgO catalyst. Significant quantities of butyronitrile were formed; but no butane was observed. When H_2 was substituted for He, butane formation was significant. We believe this is an important area which will need a more careful investigation in the future.

Our future efforts will continue in the directions outlined in the previous report, i.e., (1) to study the H_2 spillover (2) to study the effect of oxide/reduced Pt catalyst. Meanwhile, I have just received your letter along with an ASTM standard for Pt reduction. Last year, we had conducted reaction studies over calcined Pt/Al_2O_3 which were reduced at 350°C and at 500°C. Significant differences in the activity and selectivity were observed. However, we shall be studying it in the future more carefully as this seems to have become a critical parameter. We also plan to characterize the transient behavior of a freshly reduced Pt catalyst and study its deactivation (regeneration); this would be a necessary exercise before kinetic studies can be made.

Please call me if you have any comments or suggestions.

With kind regards.

Yours sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA:law

cc: Mr. Scott McMillan

TABLE 1: Performance of Modified Feed System

TEMPERATURE OF SATURATED OR T_{sv}	% BN IN FEED
0.0°C	0.63%
25°C	1.60%
35°C	2.78%
50°C	6.84%

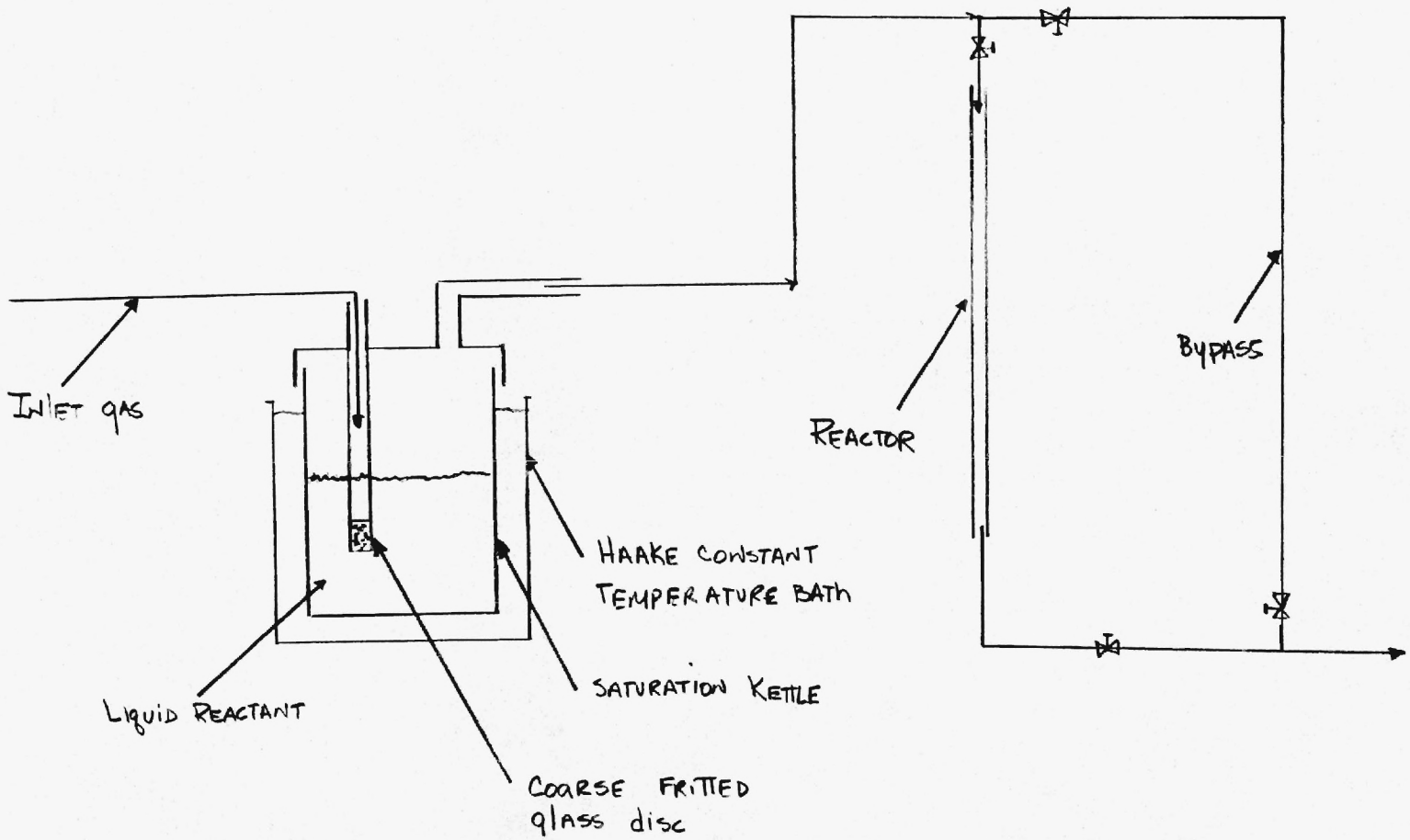

FIGURE #1: FEED MODIFICATION

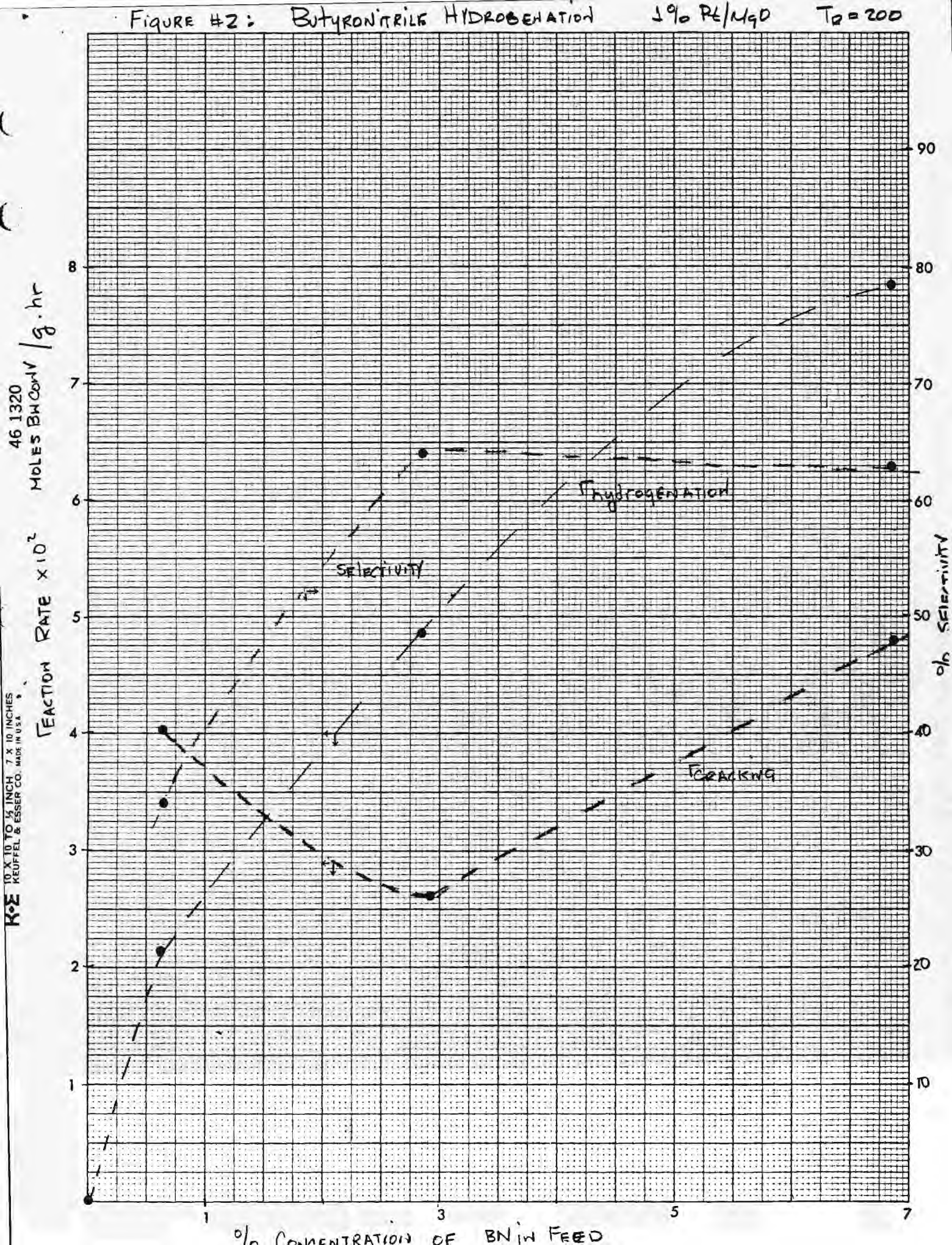
FIGURE #2: BUTYRONITRILE HYDROGENATION 1% Pt/MgO T = 200
REACTION RATE x 10²
MOLES BN CONV / g. hr
% SELECTIVITY
% CONCENTRATION OF BN IN FEED
HYDROGENATION
SELECTIVITY
CRACKING
46 1320
KEUFFEL & ESSER CO. MADE IN USA
10 X 10 TO ½ INCH 7 X 10 INCHES

E-19-65

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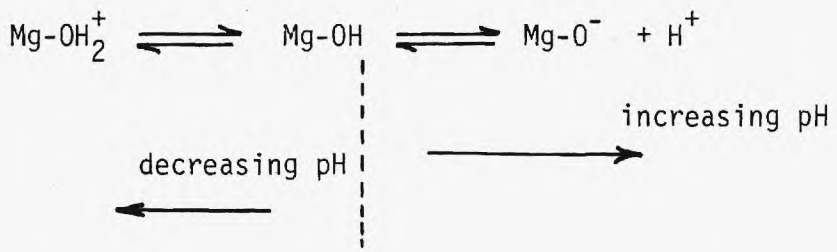
June 5, 1983

Dr. Ed Vrieland
Central Research, 1776 Building
Chemical Process Laboratory
The Dow Chemical Company
Midland, MI 48640

Dear Ed:

Please find enclosed the fourth quarterly progress report for the project entitled, "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts During Reduction of Low Molecular Weight Nitriles," covering the period of March 1, 1983, through May 31, 1983. As you would refer to our last progress report, we had proposed to vary the metal dispersion on a single support (MgO in this case), so that the effect of one variable can be eliminated and the changes in catalytic behavior can be attributed directly to the crystallite size changes, while keeping the same catalyst support. Most of our efforts during the last quarter have been directed towards this goal.

In the past, we were using the aqueous impregnation technique using hexachloraplatinic acid, but were able to get only large Pt crystallites on MgO (d = 200-300 A^{o}). In order to prepare smaller Pt crystallites, we decided to use ion-exchange technique. However, unlike acidic supports (e.g., Al_2O_3), the use of Pt $(NH_3)_4^{2+}$ complex is not feasible on a basic support (e.g., MgO). Hence, the support surface chemistry is an important factor in preparing highly dispersed Pt on MgO catalyst. A key aspect of this surface chemistry is the dissociation of hydroxyl groups on the MgO surface. The equation below indicates that by proper adjustment of pH, the MgO surface may carry a positive or a negative charge.



Here one would expect that the amion exchange of $PtCl_6^{2-}$ would be facilitated at low pH values due to the high density of $Mg\text{-}OH_2^+$ species on the MgO surface. This approach was tried in our experiments with catalyst preparation and appears to give very satisfactory results. Figure 1 shows the effect of solution pH value on the uptake of Pt (or on the metal loading on MgO). By changing the pH between 3 and 11, the metal loading can be decreased from 1.4 wt. percent to 0.1 wt. percent (one order of magnitude variation). The detailed procedure is described below.

The chloroplatinic acid was mixed with 100 cc of distilled water and was allowed to equilibrate for 1 hr. The pH was adjusted by the addition of a 10% NH_3 solution and was allowed to reach a steady value over a 60 min. period. A small sample was taken to be analyzed by atomic absorption spectrophotometry to determine the initial Pt concentration in the solution. The MgO support was then added and the solution was kept stirred at 25°C for a period of 6 hr. The slurry was then vacuum-filtered, and the filtrate was again analyzed for Pt using AA Spectrophotometry. The solid residue was then washed with 200 cc of distilled water and was dried overnight at room-temperature. The data from AA Spectrophotometry were used to determine the total Pt uptake on the MgO carrier. A typical method for the preparation of 1.4 wt % Pt is shown in Table I below.

Table I. Preparation of 1.4% Pt/MgO

Distilled Water	100 cc
$H_2Pt\ Cl_6$	0.124 gm
NH_3	2.5 cc
MgO	5.0 gm
Exchange Temperature	25° C
Exchange Time	6 hr

The sample catalyst was characterized using our new H_2 chemisorption apparatus. First, the catalyst was reduced in flowing (100 CC/min) H_2 at 350° C for 16 hr. The sample cell was then evacuated to $3X10^{-5}$ Torr at 400°C for 2 hr. Subsequently, the catalyst sample was cooled to room temperature, and then H_2 chemisorption

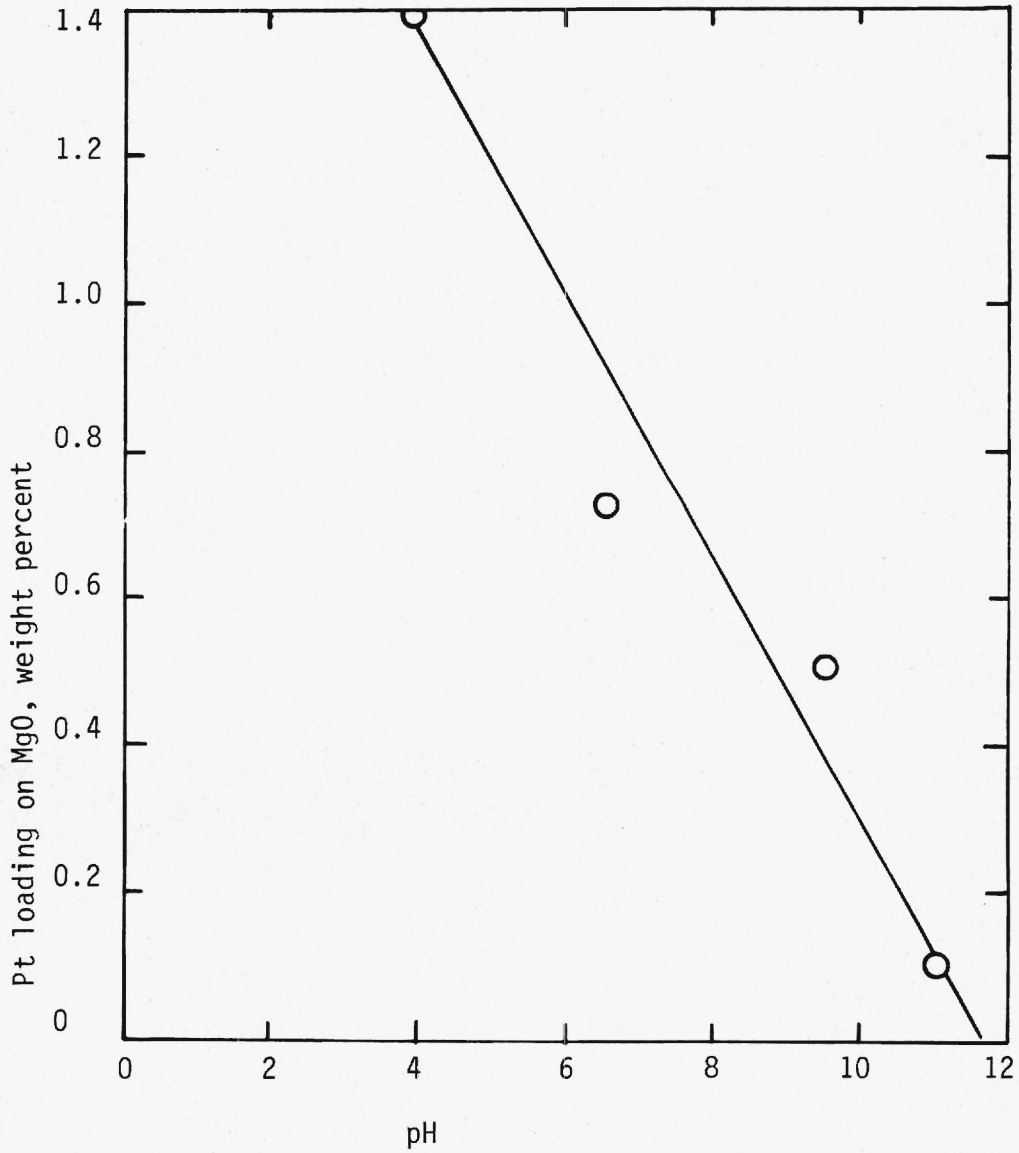


Figure 1. Effect of the pH of hexachloroplatinic acid on the uptake of Pt on MgO at 25°C.

experiment was performed. Figure 2 shows the data for H_2 chemisorbed vs. H_2 pressure. A linear extrapolation of these data to zero H_2 pressure gives the surface area corresponding to a monolayer. For 1.4% Pt/MgO shown in Figure 2, a surface of 3.61 m^2/gm is obtained; the Pt dispersion is about 96%.

The catalyst was tested in our reactor at 1 atm and at 200°C. The feed consisted of 2.9% butyronitrile (balance H_2). The steady state rate behavior is summarized in Table II.

Table II. Nitrile Hydrogenation over Ion-Exchanged 1.4% Pt/MgO Catalyst

Product	Rate $\left(\frac{\text{gmoles butyronitrile}}{\text{gCat - hr}} \times 10^3\right)$
Butyl amine	5.72
Dibutyl amine	14.71
Tributyl amine	1.50
Butane	1.17
Total Hydrogenation	21.93
Total Cracking	1.17
Selectivity =	95%

Although very high selectivity (95%) is observed, the major hydrogenation product is dibutyl amine. These results can be compared qualitatively with moderately dispersed Pt/Al_2O_3 and Pt/SiO_2 catalysts: On small Pt crystallite, the hydrogenation selectivity is shifted towards higher amines (dibutyl amine, tributyl amine). However, the rate of cracking is much lower on Pt/Mgo than on alumina - or silica - supported Pt catalysts. Apparently, the cracking reaction (butane formation) occurs predominantly on acidic support (SiO_2, Al_2O_3) and is not very significant on MgO support.

We plan to continue to characterize these ion-exchanged Pt catalysts using H_2 chemisorption, temperature-programmed reduction, and transmission electron microscopy. We also plan to study the effect of Pt particle size in the range

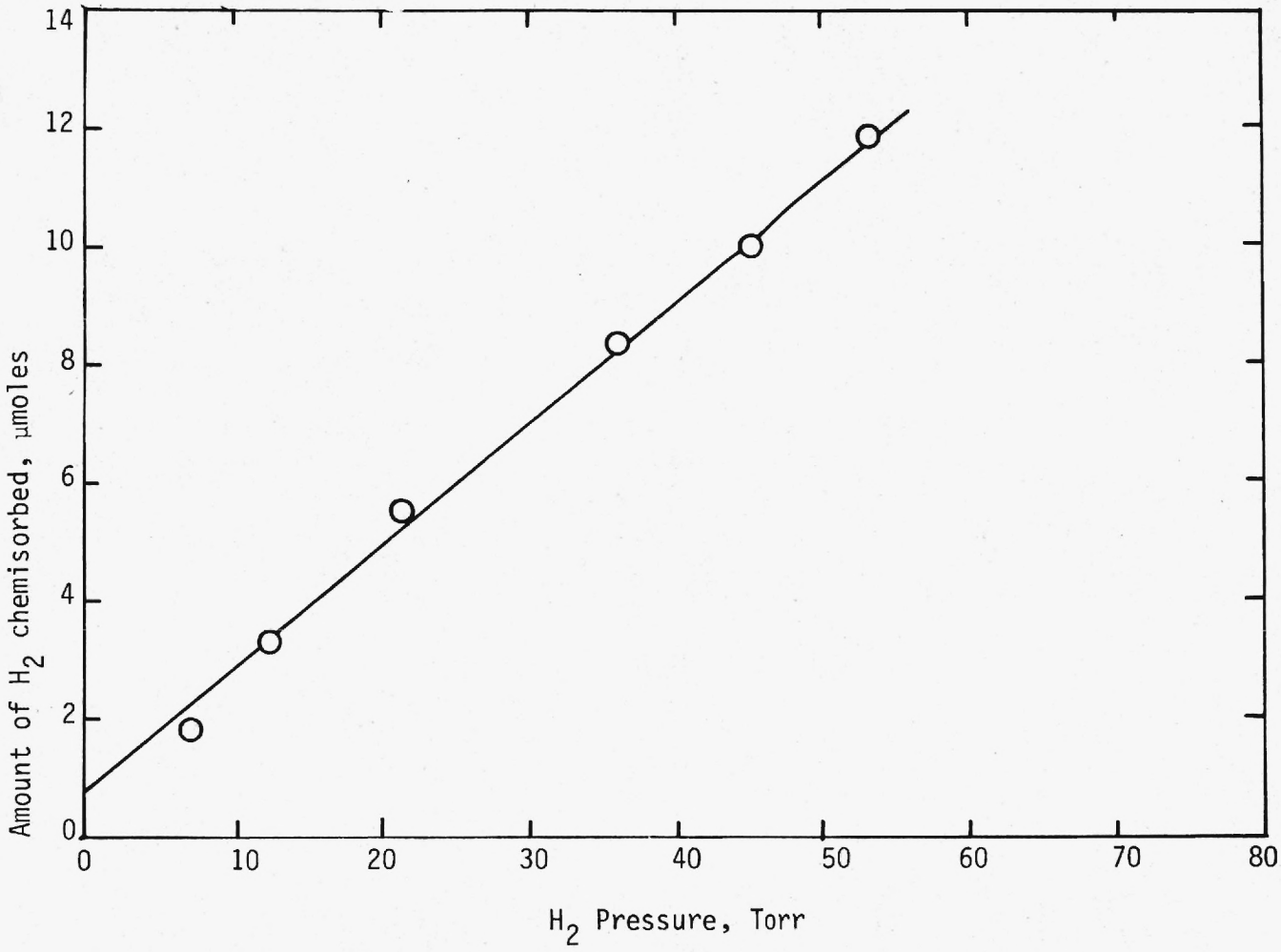


Figure 2. H_2 chemisorption isotherm for 1.4% Pt/MgO prepared by agueous ion-exchange method. The catalyst was reduced at 350°C for 16 hr and evacuated at 400°C for 2 hr prior to chemisorption

Of 10-100 A^{o} on the activity and selectivity behavior and to make kinetic measurements on these catalysts. Please call me at (404) 894-2826 if you have any questions or comments.

With best regards.

Sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA:cs

Enc.

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Georgia Institute of Technology

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SCHOOL OF
CHEMICAL ENGINEERING
(404) 894-2826

September 8, 1983

Dr. Ed Vrieland
Central Research, 1776 Building
Chemical Process Laboratory
The Dow Chemical Company
Midland, Michigan 48640

Dear Ed:

This is to update you on the work we have been doing during the period (June 1, 1983 - August 31, 1983) on the project "Hydrogenation vs. Hydrogenolysis Selectivity of Bimetallic Catalysts during Reduction of Low Molecular Weight Nitriles". In our last progress report, I had reported the preparation of Pt/MgO catalysts by ion-exchange technique. We had used this technique to prepare MgO-supported catalysts with better Pt dispersion than we had been getting by using the aqueous impregnation procedure. We had changed the Pt loading over an order of magnitude (0.1 wt percent to 1.4 wt percent) by varying the pH of the ion exchange solution between 11 and 3.

Much of our effort during the past three months has focused on the characterization of these catalysts using H_2 chemisorption measurements, and we have also tried to characterize these catalysts by temperature-programmed reduction. It is hoped that TPR studies will provide a data base to compare the catalysts prepared by different techniques or to compare the catalysts supported on different substrates.

The catalysts prepared by ion-exchanged method were dried over a 10-12 hr period in air at room-temperature; no calcination step was carried out. Subsequently, the catalysts were reduced in flowing H_2 for 10 hr at 673°K, prior to loading in the chemisorption apparatus. The hydrogen adsorption isotherm was obtained at room temperature by exposing the reduced Pt catalyst to increasing hydrogen pressure (1 Torr - 40 Torr). The extrapolated curve to zero pressure represents the hydrogen chemisorbed at a monolayer coverage. Then the catalyst cell was evacuated at room temperature for 5 min and again the adsorption isotherms were obtained. Figure 1 shows these two isotherms for one catalyst example. Since the physisorbed hydrogen should desorb during the evacuation step, the second isotherm corresponds to that of physical adsorption. The two isotherms

should be parallel to each other and the difference between them represents the amount of H_2 chemisorbed corresponding to a monolayer. We obtained reasonably good agreement between the results obtained from this difference method and the results obtained from extrapolation to zero pressure. The results are plotted in Figure 2. It is seen that over the entire range of Pt loading, the metal surface area increases linearly with the metal loading. This shows that the Pt crystallite size does not vary with metal loading; only the number of Pt crystallites change. This result is in excellent agreement with those reported by Dorling et al. (J. Catal., 20, 190, 1971). They prepared Pt/SiO_2 catalysts by ion-exchange method using H_2PtCl_6 solution and found that the Pt surface area increased linearly upto 5 weight percent Pt loading. Figure 2 shows several data points for each catalyst composition, which demonstrates the reproducibility of our measurements. The metal dispersion is calculated to be about 53% for this series of catalysts which corresponds to a mean crystallite size of about 25 A^o. This dispersion is almost an order of magnitude better than that obtained for Pt/MgO catalysts prepared by impregnation method. Future efforts to prepare even better dispersed catalyst will focus on non-aqueous preparation method, e.g. the use of acetonitrile or hydrazine.

Temperature-programmed reduction (TPR) experiments were conducted using a 1% Pt/MgO sample. The TPR profile actually corresponds to the decrease in the concentration of hydrogen (hydrogen consumption) in a stream of 1% H_2 in Ar flowing over the catalyst as the temperature is increased linearly at a rate of 20^oK/min. Figure 3 shows a TPR profile for the sample which had been dried overnight at room temperature following the ion-exchange preparation step. What we are observing in Figure 3 is a coupled effect of the signals from hydrogen consumption and the production of HCl. The negative peak indicates the production of HCl, whereas the positive peak should be indicative of the evolution of chlorine (Cl_2).

The catalyst after H_2 treatment (as shown in Figure 3) was treated with 10% O_2 in He at 623^oK for 10 hr, and then the TPR experiment was performed. This time a dry ice-acetone trap was placed between the reaction exit and the TC detector to trap out the water formed. The resulting chromatogram is shown in Figure 4. Three principal peaks (65^oC, 285^oC, and 469^oC) are observed for the reduction of Pt/MgO catalyst. We would like to compare it with the TPR profile obtained for Pt/Al_2O_3 catalyst. Figure 5 shows the results for Pt/Al_2O_3 catalyst; again three peaks (160^oC, 360^oC, and 510^oC) are obtained. A comparison of Figures 4 and 5 clearly shows that although the average Pt particle size may be similar for both catalysts (25 A^o), the Pt supported on MgO is reduced more easily as compared to that supported on Al_2O_3. This apparently indicates the degree of metal-support interaction (MgO vs. Al_2O_3). In future studies, we hope to be able to conduct these TPR experiments on MgO supported catalysts with different Pt crystallite sizes to identify the extent to which such metal-support interactions might be influenced by the particle size.

At this stage, we are moving towards conducting reaction studies with these ion-exchanged catalysts, we do not have too many results yet. For comparison purpose, the results of one experiment conducted with ion-exchanged Pt/MgO are presented in Table I which also includes the results obtained on Pt/MgO and Pt/Al_2O_3 catalysts prepared by impregnation technique. It is seen that while the high selectivity for hydrogenation is maintained on MgO-supported catalysts, the selectivity for ion-exchange catalyst is shifted towards dibutyl amine as compared to the high selectivity towards butyl amine observed over impregnated catalyst. Also this high selectivity towards dibutyl amine is in agreement with that obtained over Pt/Al_2O_3 catalysts. At first glance, it appears that the role of support may be significant in the hydrogenolysis reaction (butane formation), whereas the Pt particle size may play a more important role in the formation of primary vs. secondary amines. It is possible that terrace sites (present on big crystallites) selectively form butyl amine, and the step, kink, or corner sites (present on small crystallites) yield selectively higher amines. Our future efforts will be directed towards defining this speculation.

Rest is going well. Please call me at (404) 894-2826 if you have any questions or comments.

Kind regards.

Sincerely,

Pradeep K. Agrawal
Assistant Professor

PKA:psh

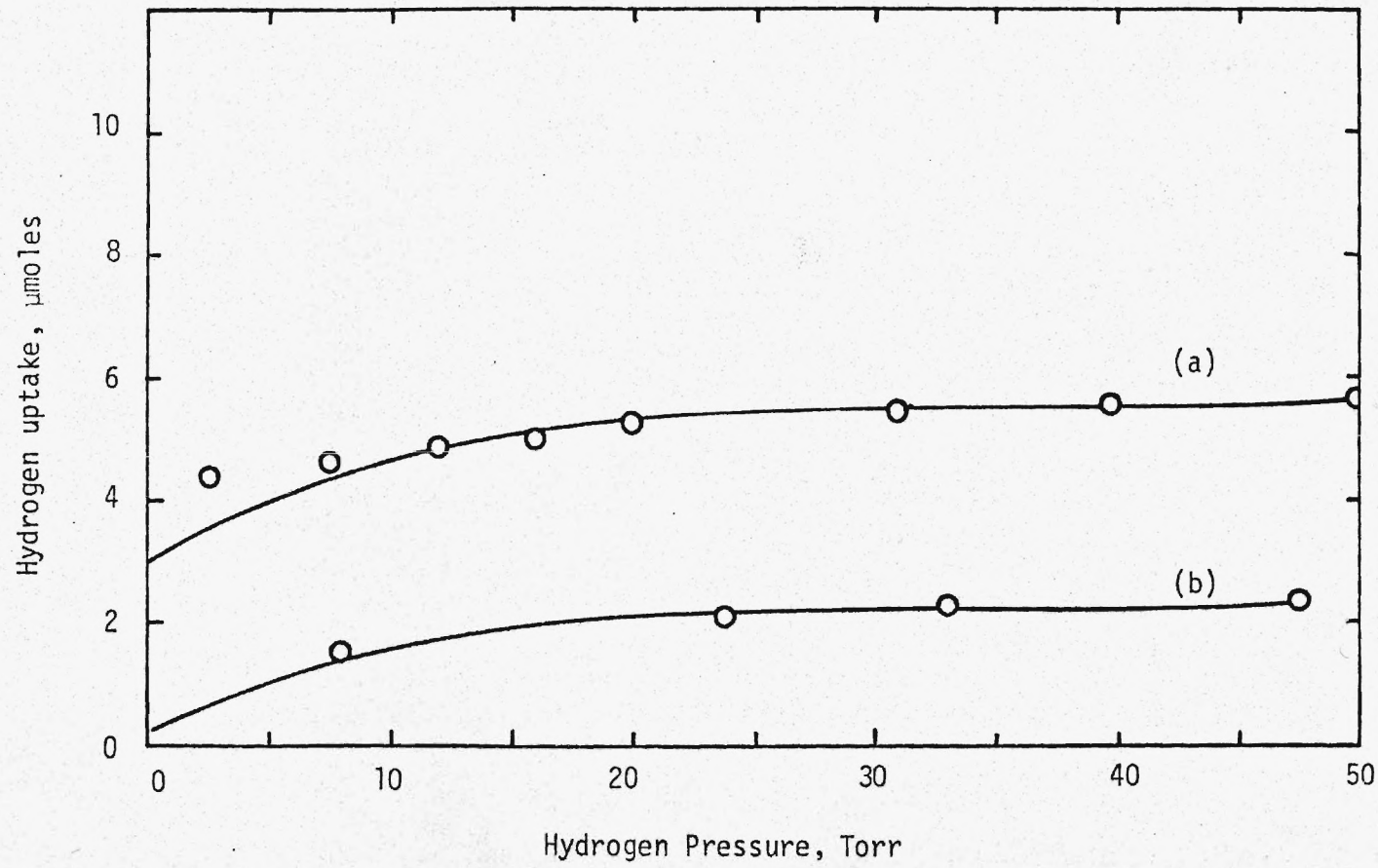

Figure 1. Hydrogen adsorption isotherms on 1% Pt/MgO at 298°K;
(a) After reduction and evacuation at 673°K overnight;
(b) After H_2 chemisorption and evacuation for 5 min at room temperature

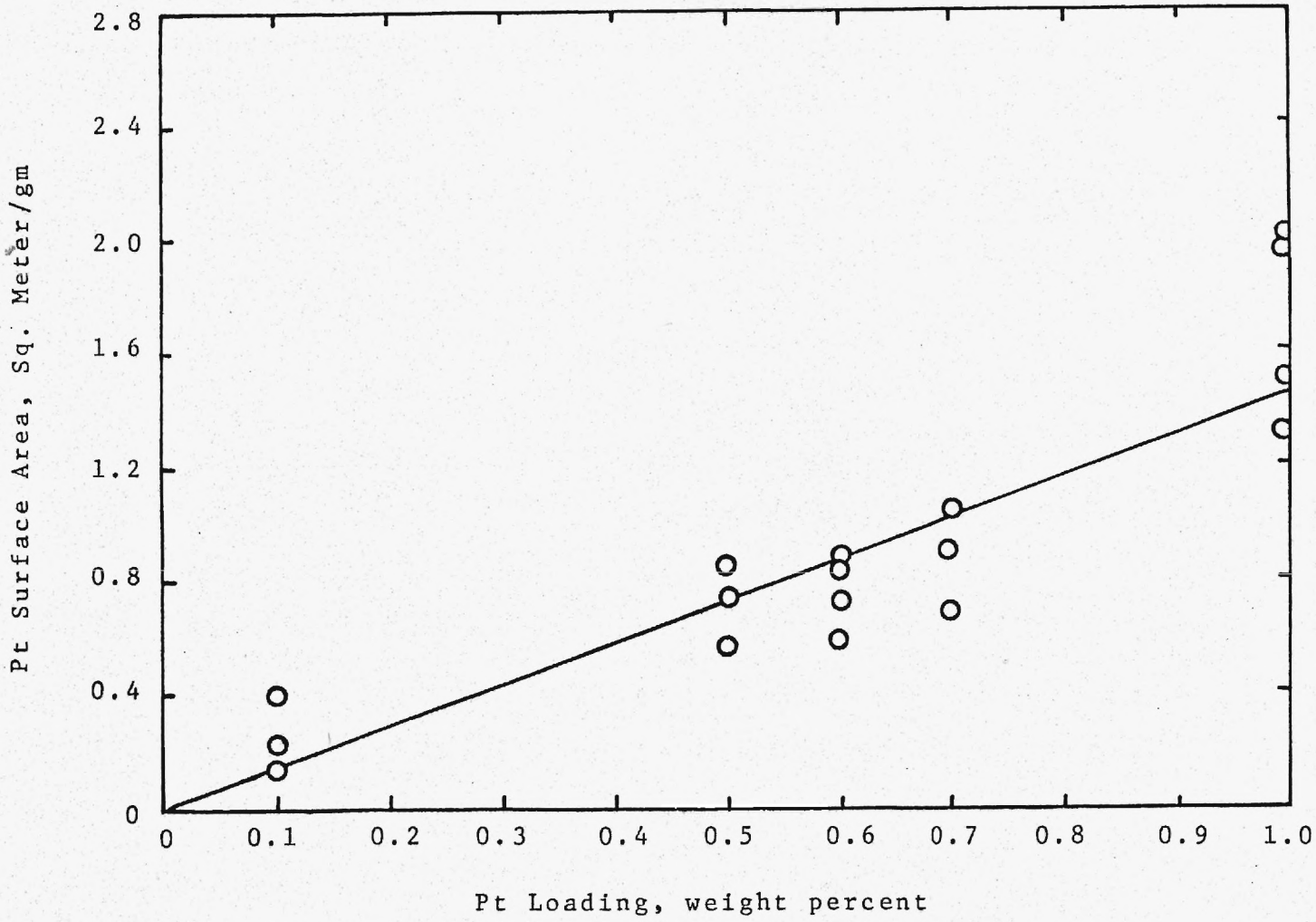

Figure 2 Effect of metal loading on the metal surface area as measured by H_2 chemisorption on MgO-supported Pt catalysts.

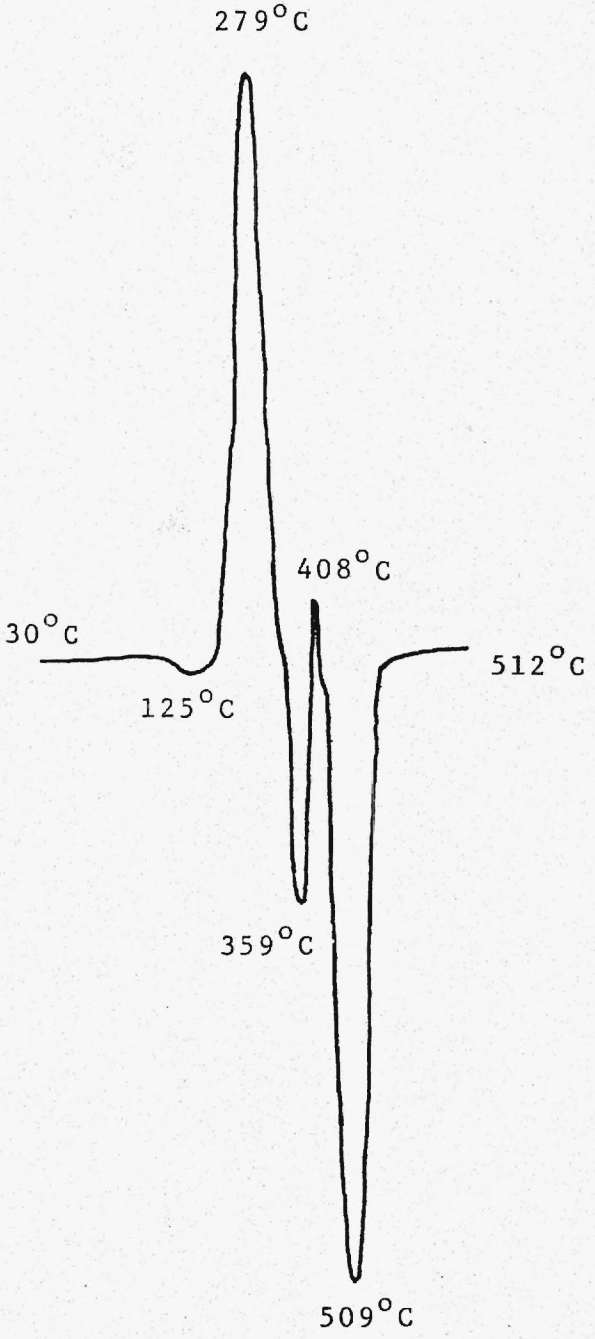

Figure 3. Temperature-programmed reduction profile of an ion-exchanged Pt/MgO catalyst. The catalyst was air-dried after ion-exchange and the profile above was obtained on untreated catalyst when it was exposed to H_2. Heating rate: 20°C/min

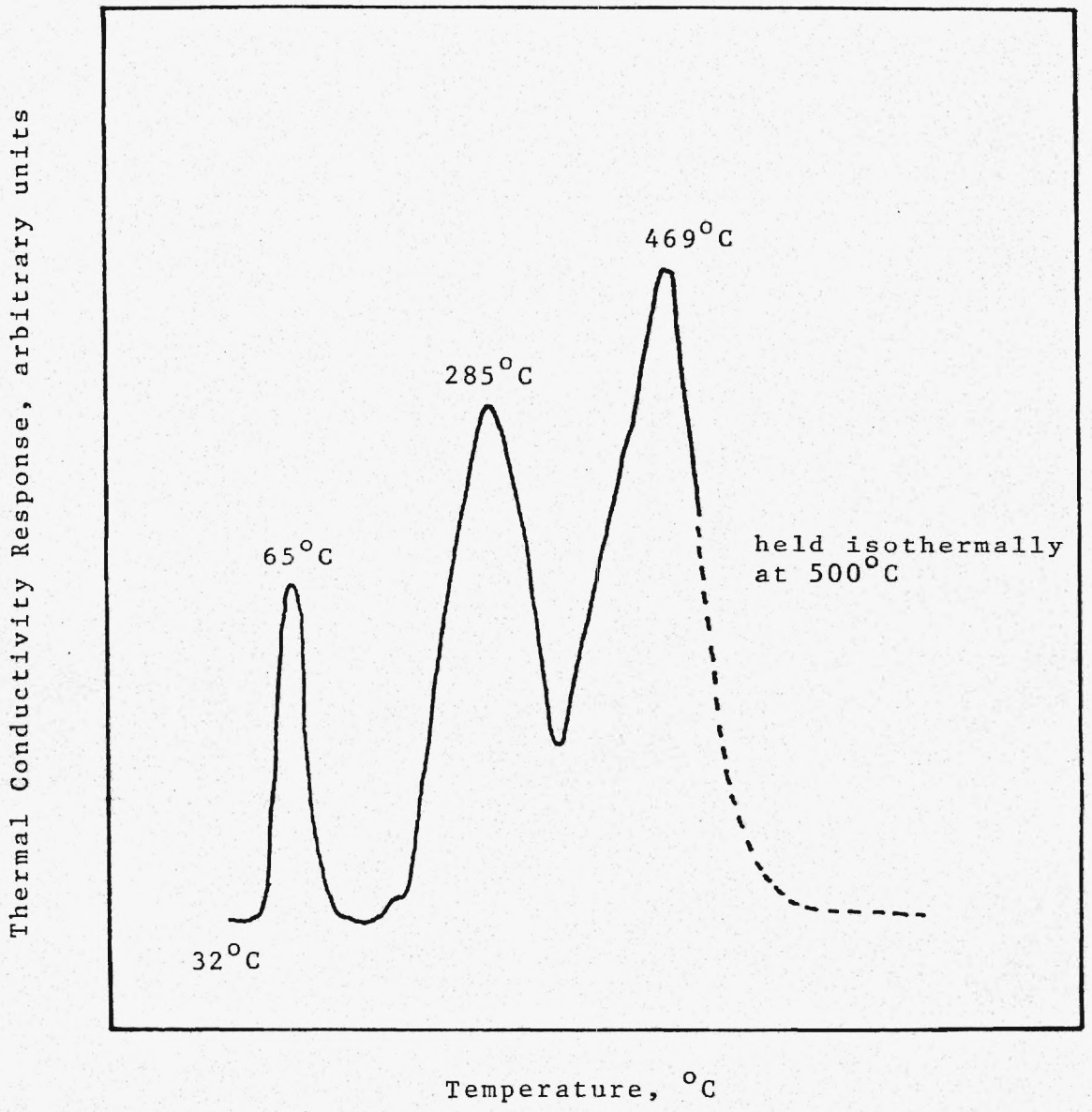

Figure 4 Temperature-programmed reduction profile of Pt/MgO catalyst prepared by aqueous ion exchange technique

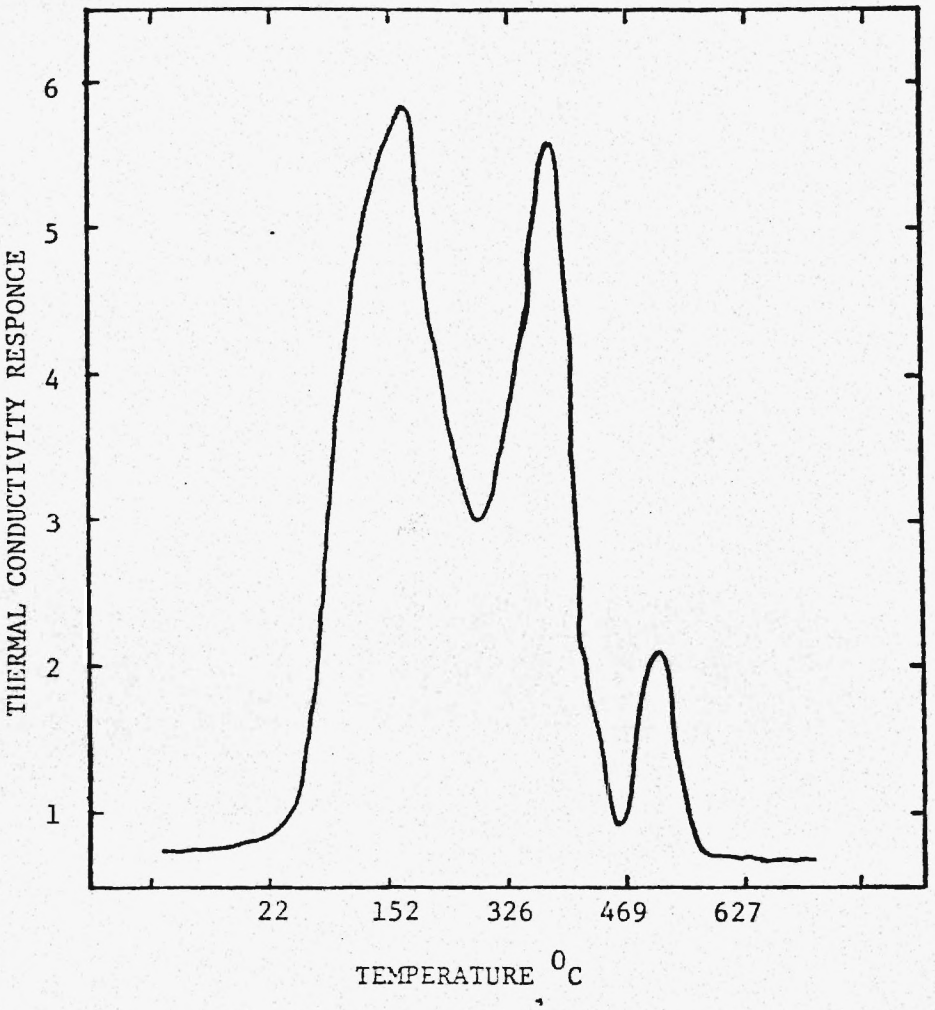

FIGURE 5: Preliminary Temperature Programmed Reduction
Catalyst: uncalcined Pt/Al_2O_3

Table I

Rates* of Cracking and Hydrogenation at 200°C, 1 atm

Catalyst	Prep. Method	Pretreatment	Rate of butyronitrile conversion, gmole butyronitrile / gm Pt - hr						Selectivity
			Butane	BA	DBA	TBA	Total Hydrogenation	Cracking	
1% Pt/MgO	Ion-exchange	H_2 at 350°C 12 hr	0.0156	0.0296	0.0791	0.0055	0.1142	0.0156	88%
1% Pt/MgO	Impregnation	H_2 at 350°C 12 hr	2.07	7.43	3.28	0	10.71	2.07	84%
1% Pt/MgO	Impregnation	Calcined, H_2 at 350°C 12 hr	0.23	0.83	---	---	0.83	0.23	78%
1% Pt/Al_2O_3	Impreg.	H_2 at 350°C 12 hr	0.90	0.25	6.7	2.7	9.65	1.15	89%
1% Pt/Al_2O_3	Impreg.	Calcined, H_2 at 350°C 12 hr	0.45	0.07	0.68	---	0.75	0.47	61%

* For ion-exchange catalyst the feed was 3% butyronitrile in H_2. For other catalysts, it was 10% butyronitrile in H_2.